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Ultraviolet Spectrophotometric Determination of Iron (III) as Acetato-complex

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The absorption spectra were investigated for the solution of ferric perchlorate at various concentration of acetic acid. A method for spectrophotometric determination of iron was studied using acetic acid as a reagent. Effects of the temperature, acidity and diverse ions were examined, and iron contents of iron base alloys were determined by the differential absorptiometry.

In order to establish a series of methods for the ultraviolet spectrophotometric determination of iron (III), especially of the methods based on differential absorptiomerty, we have already developed three mothods, in which sulfuric,[1] perchloric[2] and hydrochloric[3] acid were used as reagents. In these methods, the absorption due to the complexes formed between ferric ions and simple anions such as chloride, hydroxyl and sulfate ions were measured.

On the absorption spectra of ferric acetato-complexes and on the analytical method for the iron (III) used the acetic acid as reagent, there are few literatures, except that of V. Reiss and coworkers.[4] They studied the visible absorption spectum of iron (III) in 50 % acetic acid solution and made its spectrophotometric determiantion. The present paper is concerned with the studies on the formation of iron (III)-acetato-complex, and the application of their results to the spectrophotometric determiantion of iron (III).

Apparatus and Materials. Spectophotometric measurements were made with a Beckman Quartz Spectrophotometer Model. D.U., using 1 cm silica cells.

Two stock solutions of iron (III) of the concentrations of 100 p.p.m. and 1.000 mg/ml, respectively, were prepared by the method previously repeorted. The acetic acid was purified by distillation until it gave negative test for iron.

EXPERIMENTAL

Absorption Spectra. The absorption spectra of ferric perchlorate in 6 *M* perchloric acid and 6 *M* acetic acid solutions are shown in Fig. 1. As previously reported, the spectrum of iron (III) in the perchloric acid solution is ascribed to the presence of the ferric aquo-ions. The spectrum of iron in the acetic acid, however, is quite different from that of the ferric aquo-ion, and is considered to be due to the ferric acetato-complexes in which some absorbing species are

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mixed.

In order to investigate the effects of changes in the concentration of acetate ion and of the acidity on the spectrum, a series of the spectra was measured under the various conditions. The absorption curves are shown in Fig. 2~5.

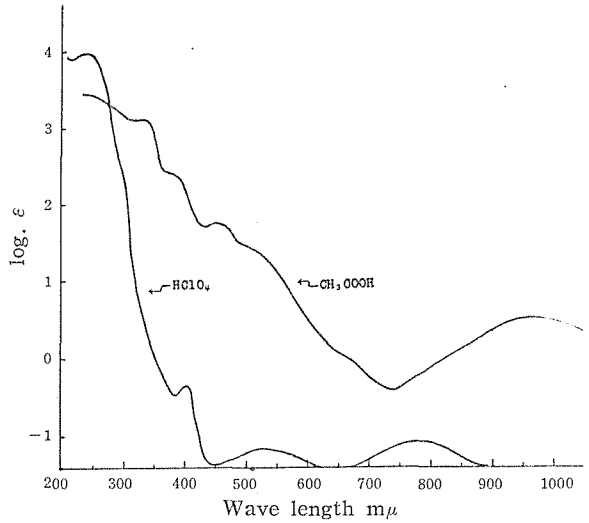


Fig. 1. Absorption spectra of iron (III) in perchloric acid and acetic acid media.

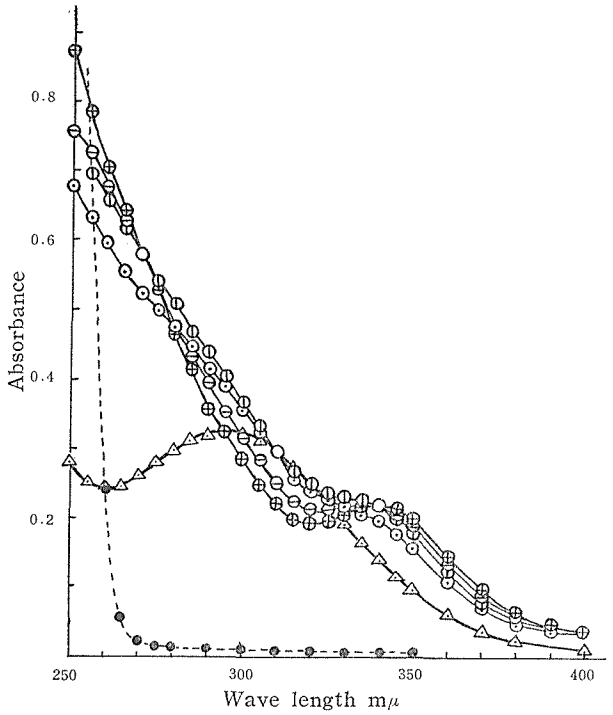


Fig. 2. Absorption spectra of ferric-acetic acid system.
—△— Fe, 10 p.p.m. (H_2O). ···●··· CH_3COOH, 15 *M*. —⊙— Fe, 10 p.p.m. ; CH_3COOH, 1 *M*. —ⓘ— Fe, 10 p.p.m. ; CH_3COOH, 5 *M*. —⊖— Fe, 10 p.p.m. ; CH_3COOH, 10 *M*. —⊕— Fe, 10 p.p.m. ; CH_3COOH, 15 *M*.

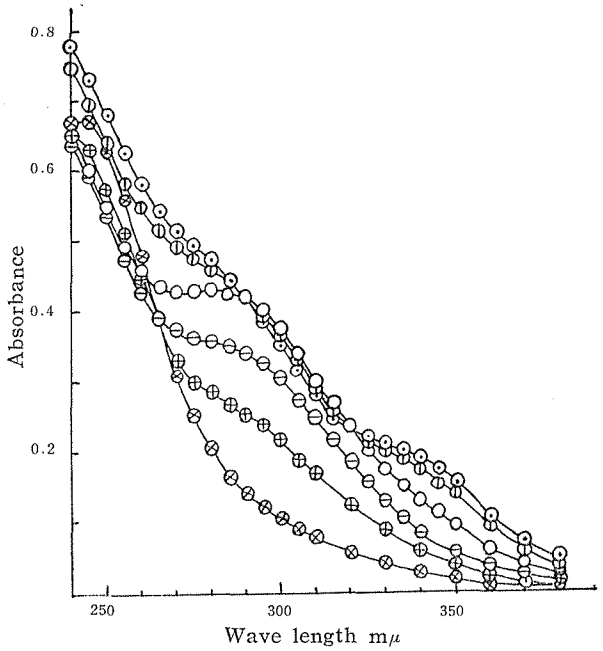


Fig. 3. Absorption spectra of ferric acetate in 1 *M* acetic acid medium.
Fe, 10 p.p.m. pH : —⊗— 1.00, —⊕— 1.41, —⊖— 1.68, —◯— 2.00, —ⓘ— 2.21, —⊙— 2.32.

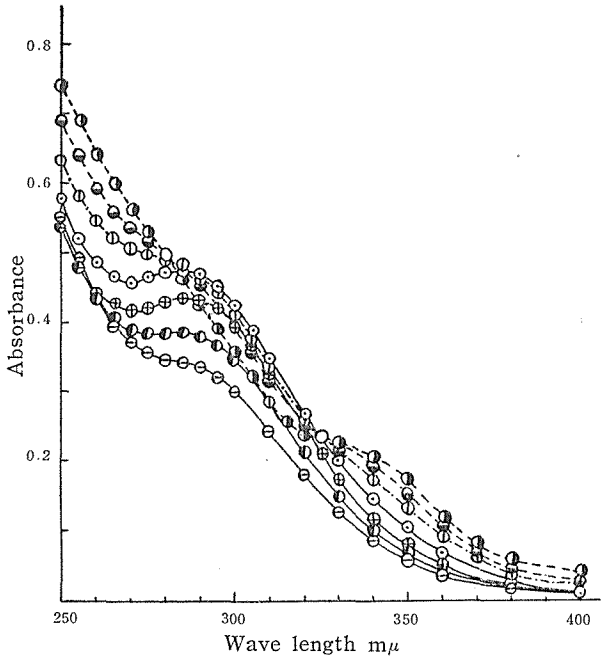


Fig. 4-a. Absorption spectra of ferric acetate in 5 *M* acetic acid medium (1).
Fe, 10 p.p.m. pH : —⊖— 0.81, —◐— 1.00, —⊕— 1.15, —⊙— 1.30, -·ⓘ-· 1.42, ···◒··· 1.60, ···◑··· 1.89.

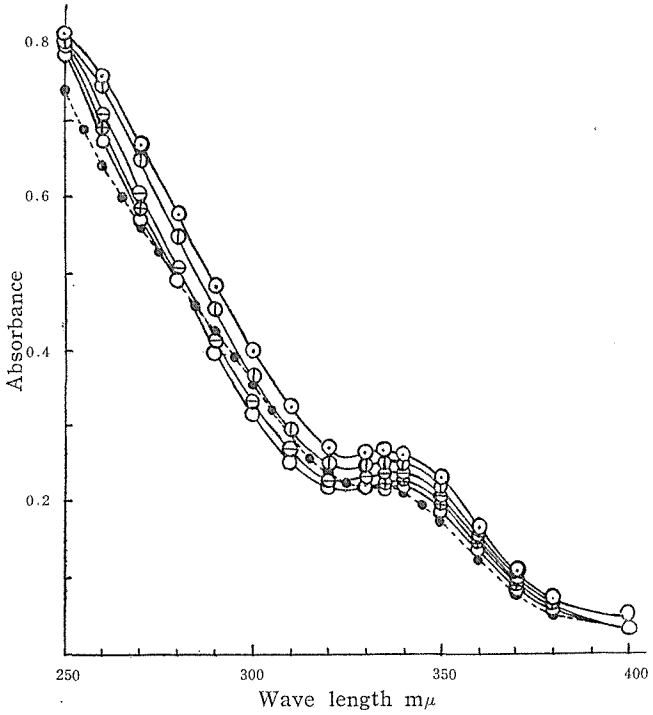


Fig. 4-b. Absorption spectra of ferric acetate in 5 *M* acetic acid medium (2). Fe, 10 p.p.m. pH : ···◉··· 1.89, —○— 2.30, —⊕— 2.81, —⊖— 3.22, —◑— 3.59, —⊙— 4.00.

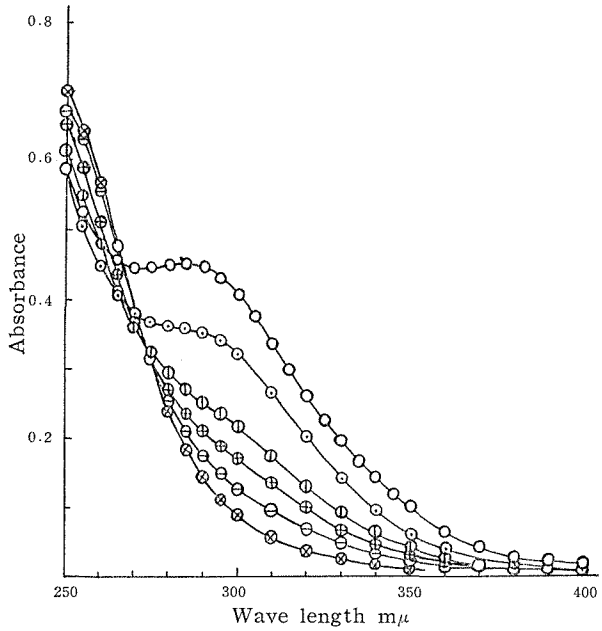


Fig. 5-a. Absorption spectra of ferric acetate in 10 *M* acetic acid medium (1). Fe, 10 p.p.m.+CH_3COOH, 10 M. $HClO_4$: —○— 0.1 N, —◉— 0.2 N, —◑— 0.4 N, —⊕— 0.6 N, —⊖— 1 N, —⊗— 2 N.

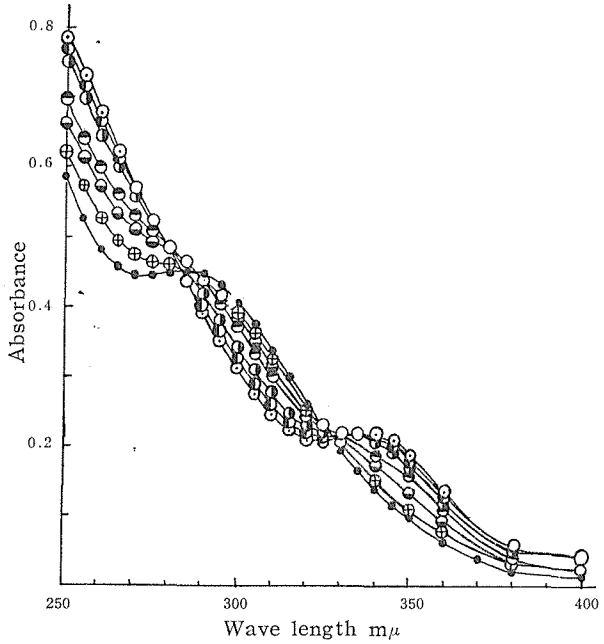


Fig. 5-b. Absorption spectra of ferric acetate in 10 *M* acetic acid (2).
Fe, 10 p.p.m. —●— $HClO_4$, 0.1 N. pH : —⊕— 0.40, —◒— 0.50, —◓— 0.60, —◑— 0.80, —◐— 1.00, —⊙— 1.21.

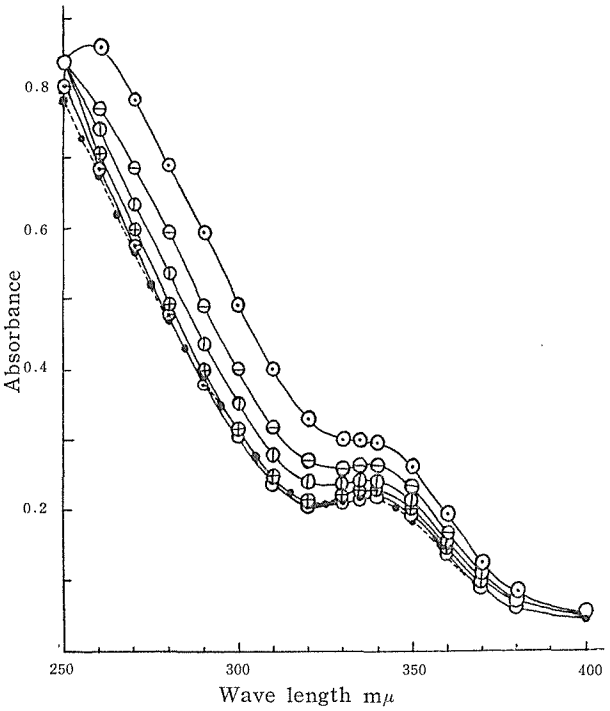


Fig. 5-c. Absorption spectra of ferric acetate in 10 *M* acetic acid medium.
Fe, 10 p.p.m. pH : ···●··· 1.21, —⊖— 1.52, —⊕— 2.21, —ⓘ— 3.10, —⊖— 3.52, —⊙— 4.42.

The discussions on these results are summerized as follows.

(1) The complicated changes of absorption spectra are due to the stepwise formation of iron (III)-acetato-complexes as represented by the equation;

$$Fe^{3+} + nAc^- \rightleftharpoons [Fe(Ac)_n]^{3-n} \qquad n=1, 2, 3, \cdots\cdots 6.$$

(2) If the acidity is considerably high, the absorption band at 290 mμ, which is characteristic of the acetato-complex, does not appear, even when the concentration of the acetic acid is very high, say 10.0 *M*. Thus, in the stronger acidic medium, the acetato complexes do not form because of the decrease of the amounts of acetate ions (Figs. 3 and 5a).

(3) It is seen from all the figures that the two absorption bands appear by the addition of the acetic acid to the ferric perchlorate solution. When the concentration of the acetic acid is high and the pH value is small, there is only a absorption band at 290 mμ. Then the amount of the acetate ion in the solution is increased either by further addition of the acetic acid or by increasing the pH values, the absorption band at 290 mμ decreases and the absorption band at 340 mμ increases. These results indicate that the band at 290 mμ is due to the formation of the lower acetato-complexes of iron (III) and the band at 340 mμ is due to the higher complexes.

(4) There are several isosbestic points in a group of absorption curves (Figs. 3, 4a, 5a and 5b). The isosbestic point at 264 mμ would suggest the presence of the equiliblium between the ferric aquo- ion and the mono-acetato-complex.

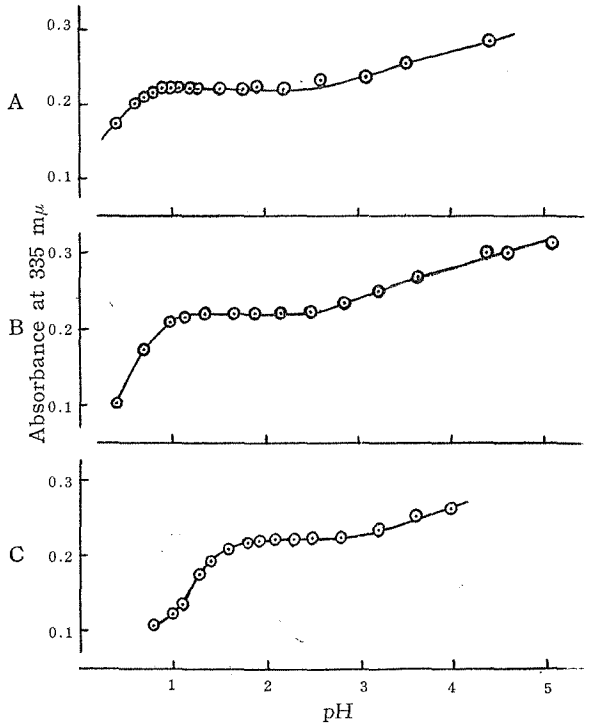


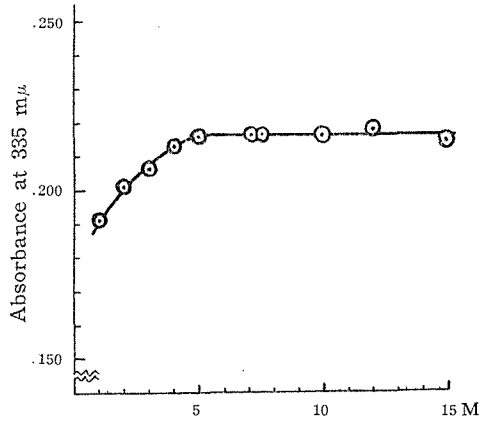
Fig. 6. The effect of pHs (Fe, 10 p.p.m.).
A : CH_3COOH, 10 *M*, ; B : CH_3COOH, 1 : 1 ; C : CH_3COOH, 5 *M*.

$$[Fe(OH_2)_6]^{3+} + Ac^- \rightleftharpoons [Fe(Ac)(OH_2)_5]^{++} + H_2O$$

The other isosbestic points at 280 mμ and 335 mμ, respectively may be attributed to the equilibrium between the lower and the higher complexes (Fig. 5b).

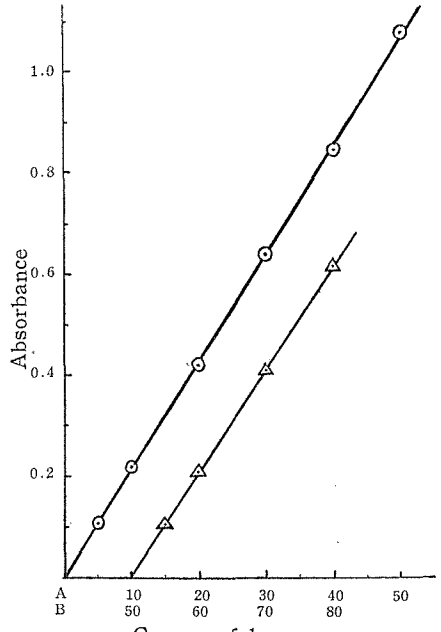
(5) When the pH value of the solution becomes higher the absorbance increases in all the range of spectra. (Figs. 5c and 4b). This may be attributed to the hydrolysis of the iron acetato-complexes.

Determination of Iron (III). The concentrations of the acetate ion and of the hydrogen ion had almost no effect on the absorbance of iron acetato-complex at 335 mμ. This is shown in Fig. 6, in which the absorbance is plotted to pH value for the various concentrations of the acetic acid. The three curves in the figure, respectively, have a horizontal range. This range has the same value in absorbance for the three curves, but shifts to the left with increasing the concentration of the acetic acid. The effect of increasing the acetic acid concentration of the absorbance is shown in Fig. 7. From this results, it is concluded that, for the determination of iron, it is not necessary to keep the acetic acid concentration constant, if the concentration is less than 5.0 *M*. The optimum range of the pH value of the solution is considerably wide, because of the buffer action of the acetate.



Concn. of acetic acid

Fig. 7. The effect of acetic acid concentration (Fe, 10 p.p.m.).



Concn. of Iron p.p.m.

Fig. 8. Calibration curves.
—⊙— Values at 335 mμ ;
—△— differential.

Calibration Curve. The standard solution of iron (III) was prepared as previously described.[2] The calibration curve was made for the ferric solutions of the concentration of 10, 20, 30, 40 and 50 p.p.m.. The solutions were prepared as follows. The proper amounts of the standard solution were pipetted into a series of 50 ml volumetric flasks. After adding 25 ml of glacial acetic

acid to each of the flasks, the solutions were diluted to the mark with water. The result followed Beer's law as shown in Fig. 8. The sensitivity of this method, however, was considerably low compared with other methods. From this result it was felt that the employment of the differential absorptiometry was necessary. Then, the calibration curve was made for the higher concentration of iron such as 50, 60, 70 and 80 p.p.m., using the concentrated ferric solution (50 p.p.m.) as a reference. In this case Beer's law was followed up to 80 p.p.m. as shown in Fig. 8. The concentrated solution of higher than 50 p.p.m. could not be used as a reference because of the decrease of the sensitivity.

Temperature. The temperature of the solution had no effect on the absorbance in the range of 10 to 35°C. This is shown in Table 1.

Diverse Ions. To study the effects of diverse ions, the cations as shown in

Table 1. The effect of the temperature.

Temperature (°C)	Absorbance at 335 mμ (Fe 10.00 p.p.m.)
9.5	0.216
14.0	.215$_5$
15.5	.215$_5$
18.0	.215$_5$
21.0	.215$_5$
25.0	.215
34.0	.215

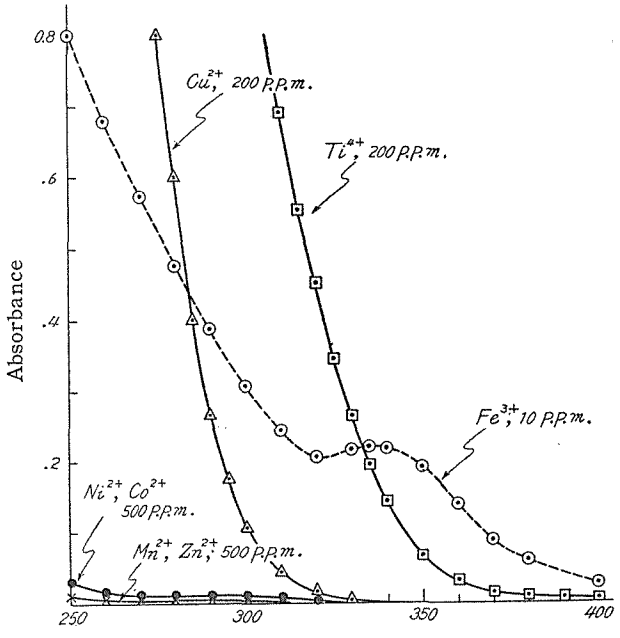


Fig. 9. Absorption spectra of diverse ions.
—◉— Ti^{4+}, 200 p.p.m. ; —△— Cu^{2+}, 200 p.p.m. ; ···◉··· Fe^{3+}, 10 p.p.m. ;
—●— Ni^{2+}, Co^{2+}, 500 p.p.m. ; —×— Mn^{2+}, Zn^{2+}, 500 p.p.m.

Table 2. The effect of the diverse ions.

Diverse ions		Absorbance at 335 mμ (Fe 20 p.pm.)
	—	0.431
Cu	250 p.p.m.	.446
Ni	〃	.463
Co	〃	.452
Zn	〃	.437
Mn	〃	.449
Ti	10 p.p.m.	.430

Fig. 9 were added as perchlorates to the acetic acid solutions and their absorption spectrum were measured. The titanium and copper ions gave intense absorption in the ultraviolet region, but the other cations had only a slight effect. To obtain the allowable concentration of the diverse ions, measurements were made for the solutions containing proper amounts of the diverse ions and 20 p.p.m. of iron. The results are presented in Table 2. It was found that the presence of such cations as Cu^{++}, Ni^{++}, Co^{++}, Zn^{++} and Mn^{++} does not interfere with the determination of iron, if their concentrations were below 100 p.p.m. For the titanium ion, the maximum allowable concentration was found to be 10 p.p.m.

Determination of Iron in Iron Base Alloy. In order to ascertain the reliablility of the method proposed above, some iron base alloys were used as samples. The determination of iron was made by means of the differential absorptiometry.

Procedure ; A 200～150 mg of sample was dissolved in 4 *M* perchloric acid by warming on the sand bath. After cooling, several drops of H_2O_2 (30 %) were added and then evaporated almost to dryness. The evaporation was repeated several times and the residue was dissolved in distilled water. The solutions was transferred to a 500 ml volumetric flask and diluted to the volume. After being mixed thoroughly, an aliquot of 20 ml was pipetted into a 100 ml volumetric flask and after adding 50 ml of glacial acetic acid, diluted to the volume with water. The absorbance of the solution was measured at 335 mμ using an iron solution (40 p.p.m.) as the reference. Results are presented in Table 3. The average error was about 0.4 %. The high value of the error for the ferro-vanadium alloy

Table 3. Analysis of iron samples.

Sample	Fe content (%) Present	Found	Relative Error (%)
Iron (J.E.S. No. 12) (low phosphor)	92.46	92.71	0.27
Haematite (J.E.S. No. 23)	61.32	61.07	0.4
Ferro-Vanadium (J.E.S. No. 19)	57,44	62.59	9.1
Ferro-Manganese (J.E.S. No. 13)	15.78	15.75	0.3

would be ascribed to the presence of vanadium (V).

SUMMARY

For the determination of iron (III), the proposed method in this report has the folloing adovantages compared with the other methods.

(1) The use of the constant concentration of the reagent is not necessary.

(2) The change of temperature has almost no effect on the absorbance.

(3) As previously reported, the interference of copper is considerably high in the determination of iron using sulfuric, perchloric and hydrochloric acids. In this method, however, its interference is almost negligible.

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